3226

ACCELERATED LIGHT-AGING STUDY OF PLASTICIZED PVC, COMPARING TWIN CARBON WITH XENON ARC

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A light-aging study was made for plasticized PVC comparing the differences between exposure to carbon arc and xenon arc. Several types of plasticizers were used. Emphasis is mainly on the changes in physical properties with respect to time of exposure.

ACCELERATED light aging by means of the xenon arc shows promise for accelerated aging, because it duplicates the spectra of sunlight better than most artificial sources. Since it is a recently introduced device, there is little information in the literature comparing the effect of the xenon arc and the standard twin carbon arc, and no study of their possible different effects, is any, on plasticized PVC. Nowacki (1962) compared the effect of these two light sources on organic coatings. A short report states that the xenon arc takes 1.2 times longer than the carbon arc for asphalts (National Bureau of Standards, 1966).

Therefore, the effect of the two types of instruments on various physical properties of plasticized PVC was studied employing several types of common plasticizers.

Experimental

The materials were all commercial compounds, selected somewhat arbitrarily but as representative of various standard types of plasticizers.

A three-component formulation of resin, plasticizer, and stabilizer was used: Geon 101, PVC [poly(vinyl chloride)] resin 65% by weight of the total mix, plasticizer 32%, G62 epoxy stabilizer 2%, and Mark M, a barium-cadmium complex stabilizer, 1%. The plasticizers were: TCP, DOP, DOZ, DOA, DOS, Drapex 4.4, G62, and Epoxol 9-5. Formulation for the epoxy plasticizers, Drapex 4.4, G62, and Epoxol 9-5, was 34% plasticizer and 1% Mark M.

Plasticizer Evaluation. Two types of accelerated light aging devices were employed, the Atlas twin carbon arc Weather-Ometer (used as a Fade-Ometer) and the Atlas 2500-watt water-cooled xenon arc Fade-Ometer with borosilicate glass filter. Samples 2.5 × 15 cm. were used for visual observations. Two strips (1 × 15 cm.) were placed side by side in a holder for determination of weight changes, torsional stiffness, and tensile properties. Samples were observed under the following conditions:

Arc	Black Panel Temp.	Air Temp., ° C.	% RH
Twin carbon	83° C. (182° F.)	60	About 5
		68	About 5
Xenon	63° C. (145° F.)	44	20
		44	50

The 83° C. temperature was the lowest we could obtain for the twin carbon arc and the instrument (an older model) lacked facilities for maintaining constant humidity. However, under test conditions the humidity remained nearly constant at about 5%.

Tensile strength, 100% modulus, elongation, torsional stiffness temperatures, T_f and T_4, volatility, and migration were measured by methods previously reported (Clash and Berg, 1942; Nieschlag *et al.*, 1964; Riser *et al.*, 1963). Volatility values were obtained at 70° C. and migration values with the sample in contact with silicic acid at 23° C.

To determine the change in torsional stiffness with respect to length of exposure, measurements were made at selected exposure times using a torsion wire apparatus (Williamson, 1950). The test samples were allowed to equilibrate for about 1 hour at 23° C. and 50% RH before stiffness readings were taken at these room conditions. The test specimens were 1 cm. wide by 10 cm. long, and the thickness of the samples varied from 0.15 to 0.18 cm. The samples were wiped dry and weighed at the time that the torsional stiffness measurements were made.

Tensile strength, 100% modulus, elongation, and T_f and T_4 temperatures were measured before starting the light exposure study and at the conclusion of exposure.

Results and Discussion

The physical properties before light aging of the molded plasticized PVC sheets are shown in Table I. The TCP sample has the highest torsional stiffness (T_f) temperature (−3° C.), very low migration and volatility losses, and the poorest heat stability. On the other hand, the DOS sample has the lowest torsional stiffness (T_f) temperature (−60° C.), highest migration loss, and moderate heat stability. The epoxidized triglyceride samples G62 and Epoxol 9–5 have moderate T_f temperatures, very low migration and volatility losses, and the greatest heat stability (32 hours). Failure determined by visual observation and the time of failure are given in Table II for each sample after light exposure in the twin carbon and xenon arcs at 83° C. (182° F.) black panel temperature with 5% RH and the xenon arc at 63° C. (145° F.) with 50% RH. The same type of failure—e.g., color change, exudate—occurred with respect to the individual plasticizer with carbon arc, xenon arc, and high or low humidity exposure. At the same test temperature 83° C. (182° F.), failure time is about the same under both the carbon and xenon arcs. At 63° C. (145° F.) with 50% RH there is a trend, as expected,

Table I. Properties of Molded Sheets of Plasticized PVC before Light Exposure

Plasticizer	*Torsional Stiffness Temp., ° C.* T_f	T_4	*Tensile[a] Strength, P.S.I.*	*Elongation, %*	*100% Modulus, P.S.I.*	*Migration Weight Loss, %*	*Volatility Weight Loss, %*	*Heat Stability (Hours to Failure) at 160° C.*
TCP	−3	−15	3120	270	1700	0.2	0.8	2.8
DOP	−31	−3	2860	300	1160	3.3	1.4	9.0
DOZ	−55	−10	2520	355	1060	18.4	2.2	9.0
DOA	−56	−19	2410	380	910	18.8	5.9	8.0
DOS	−60	−16	2420	360	970	20.4	1.5	9.0
Drapex 4.4	−47	−8	2410	360	1070	14.3	1.4	30.0
G62	−19	6	2750	360	1320	1.4	0.4	32.0
Epoxol 9-5	−12	11	2960	330	1450	0.4	0.3	32.0

[a] *Tested at 20 inches/min.*

Table II. Failure Time of Plasticized PVC from Visual Observations

Plasticizer	*Type of Failure*	*Carbon Arc, Hours at 83° C., 5% RH*	*Xenon Arc* Hours at 83° C., 5% RH	*Xenon Arc* Hours at 63° C., 50% RH
TCP	Amber with some tack	144	144	504
DOP	Spots and amber with some exudate	815	760	504
DOZ	Moderate exudate	336	384	336
DOA	Moderate exudate	600	760	504
DOS	Moderate exudate	168	168	336
Drapex 4.4	Moderate exudate	144	144	336
G62	Moderate exudate	456	384	408
Epoxol 9-5	Moderate exudate	504	600	456

at a lower temperature, toward longer exposure time before failure. The 20% RH test showed failure at somewhat longer times than at 50% RH.

After 3000 hours' exposure at 20 and 50% RH, the test was terminated, since the samples showed a significant color change, dark brown to black, or in the case of the epoxy plasticizer specimens, moderate color change, in addition to which they had become completely rigid and brittle. For the 83° C. (182° F.), light exposure under either the carbon or xenon arc the test was stopped at various times (Table III).

The effect of light aging on the torsional stiffness T_f and T_4 temperatures of these materials for the carbon and xenon arcs at the 83° C. (182° F.) test conditions is shown in Table III. Exposure time varies from 240 to 2000 hours in the twin carbon arc and 240 to 1250 hours in the xenon arc. The TCP-containing sample had the shortest exposure (240 hours). The T_f and T_4 temperature values are all higher than those of the initial unaged samples (Table I). The TCP (xenon arc) shows the smallest change, only 7° higher than the unaged sample; however, this sample also had the shortest exposure and a low loss of plasticizer.

Comparison of the T_f and T_4 values for the carbon and xenon arcs shows that they agree fairly well. The greatest differences were observed for the DOZ, DOA, and Drapex 4.4, which can be accounted for by greater volatility losses due to the higher air temperature encountered in the Xenon machine. There is a difference in that the hours of exposure required in the xenon arc to obtain these values is less, or at the same number of hours the samples are stiffer, as shown by higher temperature values (with the exception of the TCP). The longer exposure of the epoxy plasticizer samples, Drapex 4.4, G62, and Epoxol 9-5, to the carbon arc caused more crosslinking, as noted by the slope obtained from the T_f and T_4 values.

After 3000 hours' exposure at 63° C. (145° F.) black panel temperature, little difference was observed with respect to humidity for the T_f and T_4 values. Compared to the values obtained at 83° C. (Table III), with a few exceptions, there was little difference. The greatest difference was that at the lower black panel temperature there was a great increase in the number of hours (2000 to 2740) required to obtain the same degradation of flexibility. There was a significant change in the tensile strength, 100% modulus, and per cent elongation for the samples exposed to the various light-aging conditions compared to the unaged samples. The 100% modulus values were obtained for the TCP samples in all test conditions, but from only three other samples. In all other cases the elongation after aging was less than 100%.

The weight losses at 83° C. (black panel) follow the same order for both the twin carbon and xenon arcs; however, the xenon arc losses are all higher, because of the higher air temperature encountered in the xenon arc device. The greatest weight loss is 17.8% for the DOA sample exposed to the xenon arc at 83° C. (black panel) and 5% RH.

The effect at 63° C. (black panel) is lower weight loss, even though exposure time is longer. Little difference in weight loss is noted with respect to humidity (20% or 50% RH). The TCP and Epoxol 9-5 have the lowest and the Drapex 4.4 the highest weight loss. The change in torsional modulus expressed as per cent increase in modulus is shown in Table IV. In general, at 83° C. (black panel) the xenon arc produced a greater increase in modulus. One exception is the TCP sample, which showed a much greater increase after 240 hours' carbon arc exposure. Also, there was no measurable increase in modulus for the DOP sample at 240 hours' carbon arc exposure. The epoxy plasticized samples show the most noticeable changes under all the test conditions. The large increase in modulus is due to the crosslinking available through the oxirane oxygen bonds.

Table III. Torsional[a] Stiffness Temperature of Plasticized PVC after Light Exposure at 83° C. Black Panel Temperature and 5% RH

	Twin Carbon Arc			*Xenon Arc*		
Plasticizer	*Hours' exposure*	T_f, °C.	T_4, °C.	*Hours' exposure*	T_f, °C.	T_4, °C.
TCP	240	10	26	240	4	22
DOP	1000	−18	8	1000	−13	13
DOZ	1000	−41	0	1000	−30	10
DOA	1500	−27	7	1000	−13	25
DOS	2000	−28	10	1250	−26	10
Drapex 4.4	1500	−3	43	1250	11	44
G62	2000	15	48	1250	12	44
Epoxol 9-5	2000	17	48	1250	18	42

[a] *Clash and Berg ASTM D-1043.*

Conclusions

The effect of the carbon and xenon arcs on plasticized PVC was studied at a dry condition (about 5% RH) with a black panel temperature of 83° C. (182° F.). The air temperature in the xenon arc machine was about 8° C. higher than in the carbon arc machine. In addition, sam-

Table IV. Per Cent Increase in Torsional[a] Modulus of Plasticized PVC after Light Exposure at 83° C. Black Panel Temperature and 5% RH

	Hours' Exposure in Twin Carbon Arc				*Hours' Exposure in Xenon Arc*		
	240	*1000*	*1500*	*2000*	*240*	*1000*	*1250*
Plasticizer	*% Increase*				*% Increase*		
TCP	1370	...	...	...	300	...	...
DOP	0	80	...	...	10	125	...
DOZ	5	100	...	...	10	160	...
DOA	5	75	190	...	20	1230	...
DOS	10	60	55	120	35	130	190
Drapex 4.4	65	2070	2940	...	130	3650	4150
G62	30	4190	3745	6650	100	2130	3125
Epoxol 9-5	165	6190	8100	8100	400	5410	6240

[a] *Torsion wire measurement (Williamson, 1950).*

ples were exposed to the xenon arc at 20% and 50% RH at a black panel temperature of 63° C. (145° F.).

Comparison made visually with regard to color change, exudation, spotting, and stiffness showed essentially the same failure times for the carbon and xenon arcs at 83° C. (182° F.) black panel temperature. The xenon arc at the lower (63° C., 145° F.) black panel temperature required about the same exposure time as at the higher temperaature, with a trend toward longer exposure time before failure. The lower humidity (20% RH) appeared to require slightly longer exposure than the 50% RH.

The Clash-Berg torsional stiffness T_f and T_4 temperatures obtained after exposure show that less time is required in the xenon arc than the carbon arc for the same change in flexibility. Little difference was noted in the T_f and T_4 temperature for the xenon arc at the lower exposure temperature (63° C.) between the 20% and 50% RH samples.

The tensile properties give no clear-cut comparison, except for more loss of strength and elongation at the longer exposure in the carbon arc. No great difference in tensile properties was noted with respect to humidity in the xenon arc at 20% and 50% RH.

There is greater weight loss in shorter time for the samples in the xenon arc than in the carbon arc at 83° C. (182° F.), explained as mainly due to the 8° C. higher air temperature in the xenon machine. Only minor differences in weight loss are found with respect to the 20% and 50% RH conditions.

The most important aspect of this study is the change in flexibility, as seen by the per cent increase in torsional modulus. Loss of flexibility in a plasticized material limits its usefulness. The values for per cent increase in torsional modulus show that the xenon arc produces a faster rate of stiffening than the carbon arc, except for the TCP sample. No significant difference was noted between the 20% and 50% RH xenon exposure. Although failure is usually determined by sight and feel, the flexibility data show that failure occurs sooner due to stiffening in some cases. It is impossible to feel changes in a semirigid material and difficult to determine quantitatively by feel the degree of stiffening in a flexible material.

Other than visually, where the carbon and xenon arc failures are essentially the same, the xenon arc requires less time of exposure for physical degradation of plasticized PVC.

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RECEIVED for review October 24, 1968
ACCEPTED July 2, 1969